

PREPARATION OF TETRAFLUOROETHYLENE-HEXAFLUOROPROPYLENE COPOLYMER

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(54) PREPARATION OF TETRAFLUOROETHYLENE-HEXAFLUOROPROPYLENE COPOLYMER

(71) We, DAIKIN KOGYO CO., LTD., a corporation organized under the laws of Japan, of No. 8, Umeda, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed; to be particularly described in and by the following statement:—

The present invention relates to a novel process for the preparation of tetrafluoroethylene - hexafluoropropylene copolymer, and particularly to a process for the preparation of tetrafluoroethylene - hexafluoropropylene copolymer having improved properties.

In general, a crude, tetrafluoroethylene (hereinafter referred to as TFE) - hexafluoropropylene (hereinafter referred to as HFP) copolymer obtained by copolymerizing TFE and HFP has volatile components of low molecular weight, and accordingly where the copolymer is molded as it is, the occurrence of foaming can not be avoided. Therefore, to avoid such foaming process wherein the crude copolymer is sintered at about 300° to about 400°C. to remove components of low boiling point has been utilized. According to such a process, however, there is a problem that the melt viscosity of the copolymer is elevated by the sintering, and besides, where the sintering is carried out in the absence of air or under vacuum the copolymer turns brown. Furthermore, where the sintered polymer thus obtained is pelletized and then heated at about 300° to 400°C. to mold, the melt viscosity of the polymer tends to vary remarkably and accordingly its molding has to be closely controlled and even under such control the molding is accompanied by problems due to the elevation of the melt viscosity of the polymer in the course of the operation.

It is said that these problems which arise in the sintering or in the molding into pellets of the copolymer at a high temperature are generally caused by the presence of unstable end groups in the copolymer deriving from

fragments of the polymerization initiator that is used, a typical example of such an end group being the carboxyl group. To avoid the varying of the melt viscosity in the sintering or in the molding into pellet of the copolymer at a high temperature, it has also been proposed to add a small amount of metal salt such as barium chloride or magnesium chloride. However, where this is done, the effects are not necessarily found to be sufficient, and moreover the procedure is complicated and results in a deterioration in the electrical characteristics (such as volume resistivity) of the copolymer. Therefore, a completely satisfactory process has never been found.

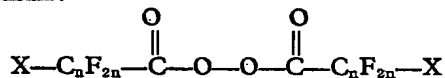
An object of the present invention is to provide a novel process for the preparation of TFE-HFP copolymer having improved properties.

Further object of the invention is to provide a process for the preparation of TFE-HFP copolymer in which the above-mentioned troubles are eliminated.

Still further object of the invention is to provide a process for the preparation of stable TFE-HFP copolymer of which the melt viscosity does not vary when the volatile component of low molecular weight contained therein is removed in the course of sintering a crude TFE-HFP copolymer obtained by copolymerizing TFE and HFP.

The other objects will be apparent from the description hereinafter and Claims.

It has now been found that these objects can be accomplished by subjecting TFE and HFP to suspension copolymerization in an aqueous medium in the presence of a di(fluoroacyl)peroxide having the general formula:



wherein X is H, F or Cl; n in case of X being H is an integer from 6 to 8, inclusive,

and X being F or Cl is an integer from 3 to 7, inclusive.

According to the process of the present invention, it is essential to carry out the suspension copolymerization of TFE and HFP in an aqueous medium as well as to use a di(fluoroacyl)peroxide having the said specific general formula as a polymerization initiator, and thereby the following remarkable advantages can be obtained. The phenomenon of the elevation of melt viscosity of the copolymer in sintering as occurs in the conventional process is completely eliminated, and the melt viscosity does not vary but is stable. The brown coloration usually obtained on sintering is also eliminated even if the sintering is carried out in the absence of air or under vacuum as in a conventional process, and any coloration does not occur in the sintering process in the presence or absence of air or under vacuum.

Fig. 1 shows an infrared absorption spectrum chart of the copolymer in the process of the present invention obtained by polymerizing TFE and HFP in an aqueous medium in the presence of di(omega - hydro - dodecafluoroheptanoyl)peroxide as a polymerization initiator.

Fig. 2 shows an infrared absorption spectrum chart of the copolymer in a conventional process obtained by employing ammonium persulfate which is known as a polymerization initiator.

As may readily be understood from Figs. 1 and 2, in case of the copolymer obtained by the process of the present invention, the absorption at 3,500, 3,080 and 1,770 cm^{-1} , due to a terminal carboxyl group is not observed in contrast to the case of the copolymer obtained by a conventional process. From this fact, it is considered that the remarkable advantages of the present copolymer are caused by the difference in the end group of the copolymer.

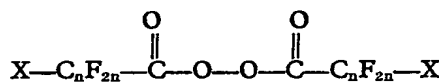
Fig. 3 is a graph showing the relationship between sintering period and melt viscosity of both copolymers. As is made clear from Fig. 3, the elevation of the melt viscosity in the course of sintering is not observed in the copolymer obtained by the process of the present invention, in contrast with that observed in the copolymer obtained by a conventional process, and the melt viscosity does not vary but is stable.

Fig. 4 is a graph showing the relationship between the heating period and the melt viscosity of both copolymers when each copolymer which is sintered and pelletized is heated at 360°C. which corresponds to the temperature in molding. As is clear from Fig. 4, no variation in the melt viscosity in the course of sintering is observed in the copolymer obtained by the process of the present invention, in contrast with that observed in copolymer obtained by a con-

ventional process, and the melt viscosity does not vary but is stable.

Hitherto it has never been known not only to use any di(fluoroacyl)peroxide having the said specific general formula as a polymerization initiator in the suspension polymerization in an aqueous medium but also to carry out the suspension polymerization of TFE and HFP in an aqueous medium in the presence of the said specific polymerization initiator. These facts are entirely new. According to the present invention, the remarkable advantages as described above, which hitherto have not been accomplished, can be obtained by the novel process. Therefore, the present invention can contribute remarkably to technical progress in this industrial field.

The polymerization initiator employed by the process of the present invention is a di(fluoroacyl)peroxide having the general formula:



wherein X is H, F or Cl; n in case of X being H is an integer from 6 to 8, inclusive, and X being F or Cl is an integer from 3 to 7, inclusive. Hereupon, both $\text{X}-\text{C}_n\text{F}_{2n}-$ groups may be straight chain or branched chain, and further may be the same or different.

Examples of the compound having the said general formula are di(omega - hydro - dodecafluoroheptanoyl)peroxide, di(omega - hydro - tetradecafluorooctanoyl)peroxide, di(omega - hydro - hexadecafluorononanoyl)peroxide, di(perfluorobutyl)peroxide, di(perfluorovaleryl)peroxide, di(perfluorohexanoyl)peroxide, di(perfluoroheptanoyl)peroxide, di(perfluorooctanoyl)peroxide, di(perfluorononanoyl)peroxide, di(omega - chlorohexafluorobutyl)peroxide, di(omega - chloro - decafluoroheptanoyl)peroxide, di(omega - chloro - tetradecafluorooctanoyl)peroxide, omega - hydro - dodecafluoroheptanoyl - omega - hydro - hexadecafluorononanoylperoxide, omega - chloro - hexafluorobutyl - omega - chlorodecafluoroheptanoylperoxide, omega - hydro - dodecafluoroheptanoylperfluorobutylperoxide, and the like.

Some of the di(fluoroacyl)peroxides having the said general formula are known compounds, and as a class these compounds tend to be easily hydrolyzed by water. Therefore, it has formerly been considered, if the compound is employed as a polymerization initiator in an aqueous medium, the initiation efficiency will be extremely low and accordingly the polymerization reaction will scarcely proceed. Although the compound has been proposed as a polymerization initiator in the case of solution polymerization or bulk poly-

merization, hitherto it has been thought that the compound can not be employed as a polymerization initiator in case of suspension polymerization in an aqueous medium, and the use of the compound in the suspension polymerization has not been described in any literature.

According to detailed research by the present inventors, it has been found that of these compounds, those in which n in case of X being H in the said general formula is 6 or more, or n in case of X being F or Cl is 3 or more can be effectively employed as a polymerization initiator in an aqueous medium because of their high stability towards hydrolysis, but those in which n in case of X being H is 9 or more or n in case of X being F or Cl is 8 or more is not only difficult to separate and purify after preparation but is also soluble only with difficulty in solvents, and therefore can not be employed for practical use.

In carrying out the process of the present invention, the amount of the said polymerization initiator employed will be optionally determined according to the ratio of TFE units and HFP units in the desired copolymer or the molecular weight. Usually, a quantity of about 0.01 to 1% by weight of the amount of monomer employed is suitable. Besides, the polymerization initiator has a relatively large decomposition velocity and its concentration tends to considerably decrease during polymerization, so that, if necessary, it may be desirable to add further initiator during polymerization.

The polymerization may be initiated by introducing water, from which air and minerals are previously removed, into an autoclave, adding TFE and HFP and further adding the polymerization initiator. In that case, the ratio of water and monomer is suitably selected from the range of about 1:1 to about 10:1, particularly about 2:1 to about 5:1 by volume.

The amount of TFE in a mixed monomer of TFE and HFP is determined according to the desired composition of copolymer shown in the following Table which may be substantiated at about 20° to 25°C.

Amount of TFE in mixed monomer (% by weight)	Content of TFE units in copolymer (% by weight)
5	78
10	87
20	92

As a reaction medium water may be employed, and, if necessary, a solvent in which TFE and HFP are soluble can also be added in a suitable amount. A preferable solvent is, for example, trichlorotrifluoroethane or monofluorotrichloromethane. If necessary, a suspension-stabilizer, e.g. polyvinyl alcohol,

sodium carboxymethyl cellulose, or a buffer such as sodium bicarbonate or borax may also be added.

The polymerization temperature is mainly determined according to the decomposition velocity of the polymerization initiator. The decomposition of the polymerization initiator in the presence of water proceeds in a form of the first-order reaction, with a velocity constant k , for example, as shown in the following Table.

	5°C.	23°C.
$[H_2CF_2CO]_2O_2$	0.031 hr ⁻¹	0.19 hr ⁻¹
$[C_2F_5CO]_2O_2$	0.043 hr ⁻¹	0.14 hr ⁻¹

Where the temperature is more 35°C., the half life period may be decreased to about 1 hour and the concentration of polymerization initiator varies widely. For carrying out a constant polymerization reaction, such a temperature is unsuitable. As a usual polymerization temperature it is suitable to select a temperature in the range of about 0° to 35°C., particularly about 0° to 28°C.

The polymerization pressure is determined in accordance with the amount of TFE and HFP employed, the presence or absence of solvent and the polymerization temperature. Where a solvent is not employed, a pressure of about 5 to about 15 kg./cm².G is generally suitable. Where a solvent, such as trichlorotrifluoroethane, is employed, a pressure of about 0.5 to about 15 kg./cm².G is suitable. The pressure varies according to the ratio of the solvent and monomer.

With the progress of the polymerization reaction, the pressure in the polymerization system is reduced. For the recovery of the pressure drop, only TFE may be added to continue the reaction. Alternatively, TFE and HFP may be added in an amount which corresponds to the consumed TFE and HFP, respectively.

The polymerization period depends on the desired yield of copolymer, and may be controlled according to the amount of polymerization initiator employed, the ratio of TFE and HFP introduced and the polymerization temperature. Usually, it may be selected from the range of about 2 to about 100 hours. During polymerization the presence of oxygen should be avoided.

When the desired yield of copolymer is reached, the residual monomers are recovered to leave a crude TFE—HFP copolymer in the form of fine powder or granular powder.

As described above, the TFE—HFP copolymer obtained by the process of the present invention has many advantages such as non-variability of the melt viscosity, high stability and resistance to colouration when sintered or when the pellet thus formed is moulded. Furthermore, the process of the present invention which is a reaction in an

aqueous system is remarkably useful in industry, in comparison with a reaction in a solvent system. Therefore, the process may be usefully utilized for the preparation of molding materials or the like.

The present invention is more particularly described and explained by means of the following illustrative examples, in which all "part" and "%" are by weight except as noted.

Example 1

An autoclave made from stainless steel (SUS 32), and having a capacity of 3,200 parts of water, provided with a jacket and a stirrer, was charged with 1,500 parts of pure water, from which air and minerals had previously been removed and 1.5 parts of sodium bicarbonate. The remaining space in the autoclave was thoroughly filled with pure nitrogen gas, and then the nitrogen gas was removed. Into the autoclave 550 parts of HFP and then 50 parts of TFE were introduced under pressure, the temperature was maintained at 25°C. and the agitation was started. To the mixture, 10 parts of di(omega - hydro - dodecafluoroheptanoyl)peroxide in 0.245 g./ml. - trichlorotrifluoroethane solution were added and the polymerization reaction was immediately initiated. During reaction, TFE is additionally introduced under pressure at a rate to overcome the incipient pressure drop so as to maintain a constant pressure. After the reaction had proceeded for 3 hours, the residual monomer was removed to produce a granular powder.

To the powder was added pure water, and the mixture was then pulverized and washed by a mixer and dried in a dryer at 70°C. for 48 hours to give 175 parts of polymer. The polymer has a HFP content of 9.7% and a specific melt viscosity of 1.27×10^6 poises.

The HFP content in polymer (%) is obtained by taking a value which is obtained by dividing the absorbance at 980 cm^{-1} by the absorbance at $2,350 \text{ cm}^{-1}$, on an infrared absorption spectrum of a film made from the copolymer to be measured and having a thickness of about 2 mils, and then multiplying the resultant quotient by 3.2.

The specific melt viscosity shown in the instant specification means an apparent melt viscosity measured at 380°C. under a shear stress of 0.457 kg./cm^2 . That is, it is given by a value which is obtained by dividing 53,150 by an extruding velocity (g./minute) measured when a cylinder, of an inner diameter of 9.5 mm., of a Koka flow tester is charged with the copolymer to be measured, the temperature of the copolymer is maintained at 380°C. for 5 minutes and then the resultant copolymer is extruded through an orifice having an inner diameter of 2.1 mm. and a length of 8 mm. under a load of 5 kg. by a piston.

As Control 1, the procedure of Example 1 was repeated except that the same molar amount of di(omega - hydro - octafluorovaleryl)peroxide was employed as a polymerization initiator instead of di(omega - hydro - dodecafluoroheptanoyl)peroxide. A specific melt viscosity for the obtained polymer is 3.1×10^5 and the yield is only 15 parts.

Where di(omega - hydro - tetrafluoropropionyl)peroxide was used, moreover, the polymerization reaction did not proceed and scarcely any yield of the desired polymer was obtained.

Though there is a difference according to the value of n as described above, the same relationship was confirmed where X is F or Cl.

As Control 2, an autoclave made from stainless steel, with a capacity of 4,000 parts of water and provided with a jacket and a stirrer, was charged with 1,500 parts of pure water from which ions and air had previously been removed and 15 parts of



as an emulsifier. After the remaining space within the autoclave had been evacuated, 300 parts of HFP were added under pressure and the temperature was raised to 80°C. Then, 80 parts of TFE were added, and the agitation was started. After 30 minutes, a solution obtained by dissolving 5 parts of ammonium persulfate in 50 parts of pure water was added under pressure. As the pressure began to fall immediately, TFE was successively added under pressure so as to maintain the initial pressure level. The polymerization reaction was continued for 12 hours, and thereafter gaseous materials were removed and then the autoclave was opened, the product being a milky and semi-transparent aqueous suspension. 800 parts of acetone were slowly added with vigorous agitation to result in the isolation of the polymer. After the filtration, the polymer was washed with water and dried to give 510 parts of a white powdery polymer.

The polymer has a HFP content of 10.6% and a specific melt viscosity of 1.4×10^6 poises.

The infrared absorption spectra of the polymers obtained in Example 1 and in Control 2 were measured and the results are shown in Figs. 1 and 2, respectively.

As is clear from Figs. 1 and 2, the polymer of Control 2 shows absorptions due to the end carboxyl group at 3,500, 3,080 and $1,770 \text{ cm}^{-1}$, but in the polymer of Example 1 these absorptions are not observed.

Both polymers were sintered at 360°C. in a nitrogen stream. As a result, the polymer of Control 2 turned black, but in the polymer of Example 1 no discoloration was observed.

Also both polymers were sintered at 340°C. in air, and the variation of their melt viscosities was measured. The results are shown in Fig. 3.

- 5 As is clear from Fig. 3, in the polymer of Control 2 the melt viscosity increased remarkably during the heating, but that of the polymer of Example 1 scarcely varied. Therefore, it can be appreciated that the
10 latter polymer has excellent stability.

Example 2

- The procedure in Example 1 was repeated except that 30 parts of di(omega - hydro -
15 dodecafluoroheptanoyl)peroxide in 0.245 g./ml. - trichlorotrifluoroethane solution were employed and the polymerization was carried out for 2.5 hours.

- A yield of the polymer thus obtained is 280 parts, and the polymer has a HFP content of 8.9% and a specific melt viscosity of
20 1.02×10^5 poises.

- As Control 3, an autoclave made from stainless steel, with a capacity of 4,000 parts of water and provided with a jacket and a
25 stirrer, was charged with 1,500 parts of pure water from which air and minerals were previously removed. The remaining space was completely filled with HFP and 300 parts of HFP were added under pressure. The reaction vessel was heated at 95°C., and then a
30 solution obtained by dissolving 0.15 part of ammonium persulfate in 20 parts of pure water was introduced. After the agitation had been carried out for 15 minutes, 80 parts of TFE were added under pressure and at the
35 same time a 5% aqueous solution of ammonium persulfate was continuously added under pressure at a rate of 1.1 parts/minute. Immediately, the polymerization reaction was initiated and as a result the pressure dropped off. TFE gas containing 8% HFP was then
40 added under pressure so as to maintain the initial pressure. This was continued for 80 minutes. Gaseous materials were removed and then the autoclave was opened, the product being a white aqueous suspension. 800 parts of acetone were slowly added with vigorous
45 agitation, resulting in the isolation of the polymer. After the filtration, the polymer was washed with water and dried to give 420 parts of white powdery polymer. The polymer has a HFP content of 13.3% and a specific
50 melt viscosity of 4.9×10^4 poises.

- Both polymers were sintered at 360°C. in
55 air, and the variation of their melt viscosities was measured. The results are shown in Fig. 3.

- As is clear from Fig. 3, in the polymer of Control 3 the melt viscosity increased remarkably on heating, but that of the polymer of Example 2 scarcely varied. Therefore, it can be appreciated that the latter
60 polymer has excellent stability.

Also both polymers were sintered at

360°C. for 2 hours in air and then pelletized, and the variation of melt viscosities at 360°C. in air was measured. The results are shown in Fig. 4.

As is clear from Fig. 4, in the polymer of Control 3 the melt viscosity increased
70 remarkably on heating, but that of the polymer of Example 2 scarcely varied. Therefore, it can be appreciated that the latter polymer has excellent stability.

Example 3

The procedure in Example 1 was repeated except that the same molar amount of di(perfluorobutyryl)peroxide was employed.

The yield of the polymer thus obtained is 156 parts, and the polymer has a specific
80 melt viscosity of 1.1×10^6 poises.

Example 4

The procedure in Example 1 was repeated except that 15 parts of di(omega - hydro -
85 hexadecafluorononanoyl)peroxide in 0.105 g./ml. - trichlorotrifluoroethane solution were employed.

The yield of the polymer thus obtained is 182 parts, and the polymer has an HFP content of 9.4% and a specific melt viscosity of
90 6.8×10^5 poises.

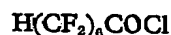
Example 5

The procedure in Example 1 was repeated except that 25 parts of di(perfluorooctanoyl)-
95 peroxide in 0.077 g./ml. - trichlorotrifluoroethane solution were employed.

The yield of the polymer thus obtained is 225 parts, and the polymer has an HFP content of 9.6% and a specific melt viscosity of
100 9.0×10^5 poises.

Example 6

The procedure in Example 1 was repeated except that 8 parts of mixed di(fluoroacyl)-
105 peroxide in 0.235 g./ml. - trichlorotrifluoroethane solution obtained by reacting an equimolar mixture of



and



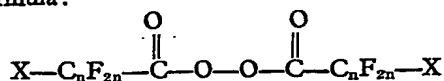
with sodium peroxide was used and the polymerization was carried out for 5.5 hours.

The yield of the polymer thus obtained is 160 parts, and the polymer has an HFP content of 9.2% and a specific melt viscosity of
115 1.7×10^6 poises.

WHAT WE CLAIM IS:—

1. A process for preparing tetrafluoroethylene - hexafluoropropylene copolymer which comprises subjecting tetrafluoroethylene and hexafluoropropylene to polymeriza-
120

tion in an aqueous medium in the presence of a di(fluoroacyl)peroxide having the general formula:



- 5 wherein X is H, F or Cl; n in case of X being H is an integer of 6 to 8, inclusive, and in the case of X being F or Cl is an integer of 3 to 7, inclusive.
- 10 2. A process according to Claim 1, wherein the said di(fluoroacyl)peroxide is at least one member selected from the group consisting of di(omega - hydro - dodecafluoroheptanoyl)peroxide, di(omega - hydro - tetradecafluorooctanoyl)peroxide, di(omega - hydro - hexadecafluorononanoyl)peroxide, di(perfluorobutyryl)peroxide, di(perfluorohexanoyl)peroxide, di(perfluoroheptanoyl)peroxide, di(perfluorooctanoyl)peroxide, di(perfluorononanoyl)peroxide, di(omega - chloro - hexafluorobutyryl)peroxide, di(omega - chloro - decafluorohexanoyl)peroxide, di(omega - chloro - tetradecafluorooctanoyl)peroxide, omega - hydro - dodecafluoroheptanoyl -
- 25 omega - hydro - hexadecafluorononanoylperoxide, omega - chloro - hexafluorobutyryl - omega - chloro - decafluorohexanoylperoxide and omega - hydro - dodecafluoroheptanoyl - perfluorobutyrylperoxide.
- 30 3. A process according to Claim 1, wherein the said di(fluoroacyl)peroxide is employed in an amount of from 0.01 to 1% by weight of the weight of the monomer employed.
- 35 4. A process according to Claim 1, wherein the ratio of water and monomer is from 1:1 to 10:1 by volume.
5. A process according to Claim 1, wherein the ratio of water and monomer is from 2:1 to 5:1 by volume.

6. A process according to Claim 1, wherein the polymerization is carried out in the presence of a solvent in which both tetrafluoroethylene and hexafluoropropylene are soluble.

7. A process according to Claim 6, wherein the said solvent is trichlorotrifluoroethane or monofluorotrichloromethane.

8. A process according to Claim 1, wherein the polymerization is carried out at a temperature of 0° to 35°C.

9. A process according to Claim 1, wherein the polymerization is carried out under a pressure of 5 to 15 kg./cm².G.

10. A process according to Claim 1, wherein the polymerization is carried out under a pressure of 0.5 to 15 kg./cm².G. in the presence of trichlorotrifluoroethane.

11. A process according to Claim 1, wherein the polymerization is carried out for from 2 to 100 hours.

12. A process according to Claim 1, wherein tetrafluoroethylene is added so as to maintain a constant pressure in the process.

13. A process according to Claim 1, wherein tetrafluoroethylene and hexafluoropropylene are added in amounts which correspond to the consumed tetrafluoroethylene and hexafluoropropylene, respectively.

14. A process according to Claim 1, wherein the polymerization is carried out in the absence of oxygen.

15. A copolymer obtained according to the process of Claim 1.

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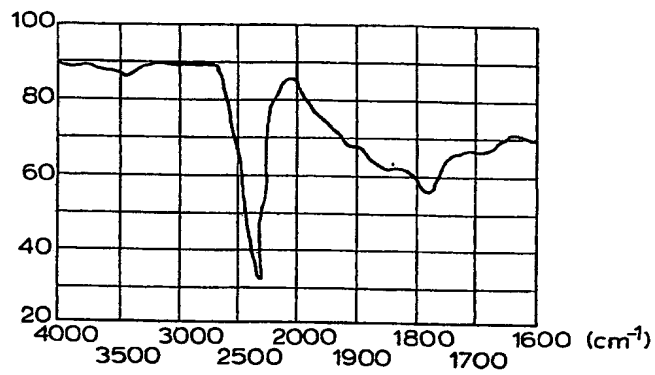


Fig.1.

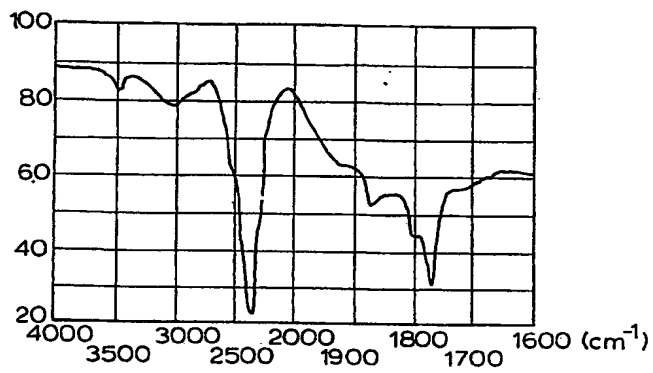


Fig.2.

